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Effects of activation schemes on porous, surface and thermal properties of activated carbons prepared from cotton stalks**

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Keywords:

activated carbon; cotton stalks; activation scheme; porosity; sem, tg, flir

Abstract

Cotton stalks were used to obtain activated carbons by one-step processes using both chemical activation by H_3PO_4 or KOH , and thermal activation by steam pyrolysis. Porosity characteristics were determined from analysis of N_2 adsorption isotherms using both BET and Langmuir equations as well as α_s and t methods. The results showed that the lignocellulosic content of cotton stalks was carbonized via different suggested mechanisms depending mainly on the activating agent. Highly to good porous carbons were obtained and the porosity increased in the order $\text{KOH} > \text{H}_3\text{PO}_4 > \text{steam}$. For the acid-activated series, the best porous carbon that having S^a of $841 \text{ m}^2/\text{g}$ was obtained from the acid-to-stalks ratio of 3:4 by weight. The biggest KOH -ratio of 3:1 gave a carbon with much higher microporosity and the biggest specific surface area among those prepared carbons ($S^a = 1307 \text{ m}^2/\text{g}$). Cotton stalks showed a good response to a single-step steam activation. Steam treatment at 600°C resulted in a limited developed porosity, whereas, an increase in temperature to 700°C led to a considerable increase in porosity and yielded a carbon of $S^a 722 \text{ m}^2/\text{g}$. Thermogravimetric study showed that acid-treatment shifts the main decomposition of cotton stalks to much higher temperatures indicating an increase in thermal stability and carbon yield. SEM and FTIR investigations evidenced that the presence of opened-pore structure and different functionalities on the carbon surfaces based, principally, on the activation scheme. The results showed also that cotton stalks, as low cost, is well suited to produce high quality activated carbons composed of a wide range of porosity that could achieve high removal capacity to a broad range of pollutants.

1. Introduction

The use of activated carbons for removing substances from either gaseous or liquid solutions has been widely used long times ago. It is well known that activated carbons can be prepared using a variety of raw materials. The most commonly used precursors are coal, wood, coconut shells and agricultural by-products. It has been shown that activated carbons obtained from agricultural by-products can be favourably compared with other activated carbons used in industry with respect to their adsorptive properties, cheap and annually renewable sources. There are numerous research results on this subject^[1-10].

For many years, cotton is considered as the number one crop in Egypt. An increasing areas of this vital crop permitted a huge amount of cotton stalks which amounts about three million tons per year^[11]. These big quantities of stalks become an environmental problem, especially after they have lost their importance as fuel, and do not give good results in paper making industries. Consequently, there is an urgent need to identify new uses for cotton stalks by converting them to good quality activated carbon, simultaneously solving an environmental problem.

In practice, there are mainly two methods for producing activated carbons: first, physical or thermal activation involves a two-step scheme by the carbonization of a carbonaceous precursor followed by activation of the resulting char with oxidizing gases such as carbon dioxide or steam in the range of 700 °C to 1100 °C. Second, chemical activation consists of a single-step scheme through carbonization at a relatively low temperature 400 – 700 °C in presence of chemical dehydrating agents such as H_3PO_4 , ZnCl_2 , or KOH . Among the numerous chemical activating agents, phosphoric acid and potassium hydroxide are widely used and preferred; the use of zinc chloride has declined in the last years due to problems of environmental contamination. Single step activations whether through chemical or thermal schemes consider the best technologies to manufacture activated carbons^[2-5,9,12,13]. They realize many recommending aspects: (i) it is a single-step with respect to heat treatment (ii) it is conducted at low temperatures saving thus energy consumption (iii) it restricts gaseous evolution and thus enhances carbon yield. In the last decade, a single-step steam pyrolysis was proposed and applied by many authors^[4,5,14]. It acquires an additional prominent feature where it is conducted without any chemicals thus saving chemicals, energy and time. So, the use of one step-method for preparation of activated carbons is considered to be economic route to realize this target.

A lack of sufficient scientific information about the utilization of this raw material for carbon production besides the huge production of such agricultural waste materials was the driving force for the choice of cotton stalks for this work. The present investigation reports preparation and characterization of activated carbons derived from cotton stalks using single-step activation schemes. This involves chemical activation with H_3PO_4 or KOH , and thermal activation with single-step steam pyrolysis. In addition we have used a new oven heating scheme in the carbonization step to avoid the possible re-adsorption of tarry material aiming to achieve fine-cleaned and developed pore structure. Variety of techniques including Fourier-transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA), and scanning electron microscopy (SEM) have been used.

2. Materials and methods

2.1 Preparation of activated carbon adsorbents

Activated carbons were prepared by treating a known weight of dried, cleaned and crushed cotton stalks (1-3 mm) with different concentrations of H_3PO_4 to provide H_3PO_4 -to-stalks ratios of 1:2, 3:4 and 1:1 by weight. The acid impregnated samples were dried overnight at 110°C till constant weight then carbonization process was carried out under the conditions as indicated in Table 1. The obtained carbons were designated as P12, P34 and P11, respectively. In a similar manner, KOH in the form of pellets was thoroughly mixed with the cotton-stalks straw in a least amount of water to provide KOH -to-stalks ratios 1:1, 2:1 and 3:1 by weight. The treated samples were then pyrolysed under the

conditions indicated in Table 1 to obtain K11, K21, K31 respectively. Char sample, C550, was prepared by carbonization of the cotton stalks at 550 °C for 3 h in a flow of nitrogen.

For all prepared carbon samples, a new oven heating scheme was carried out in two sequential stages. At the starting stage the heating rate was 5 °C min⁻¹, up to 250 °C, and the sample was held at this temperature for 1 h. In the second stage, the oven was heated to reach to the pre-determined final temperature then held until the designated time of carbonization and/or activation (Table 1). During the entire heating process, a nitrogen gas flow rate 50 ml min⁻¹ was flowed through the reactor tube. This step was introduced to prevent the re-adsorption of tarry materials and to give a sufficient time for complete removal of all volatile matter of low and medium sizes, such as water, alcohols, and acetic acid. Finally, a washing process was carried out for acidic samples using a solution of 0.1 mol dm⁻³ NaOH, and for basic samples with a solution of 0.1 mol dm⁻³ HCl. All the prepared carbon samples were thoroughly washed with hot distilled water until the pH of the washings was about pH7.

2.2 Textural and chemical characterization

Textural properties were deduced from the adsorption isotherms of N₂ at 77K using a porosimeter (Micromeritics, ASAP-2010). Prior to measurement the samples were degassed under vacuum at 350°C and pressure 10-5 Torr for 4 h. Analysis of the adsorption isotherms was carried out by applying Langmuir and BET equations to get SBET, SL and total pore volume, VP, from nitrogen held at a saturation relative pressure. An average pore radius was also estimated from the relation

$$r \text{ (nm)} = 2V_p 1000 / SBET$$

The micropore volume was calculated from the amount of N₂ adsorbed at a relative pressure of 0.1, and mesopore volume was evaluated by subtracting the amount adsorbed at a relative pressure of 0.1 from that at a relative pressure of 0.95 [2]. More useful information about the surface characteristics was obtained by applying α_s - and t-plots, which provide a simple means of comparing the shape of a given isotherm with that of a standard non-porous solid. Hence the α_s - method was employed using the standard data reported by Sells-Perze and Martin-Marteneze [15]. From a plot of volume of N₂ adsorbed, V_{ads} against α_s values, four parameters were obtained: the total or apparent surface area, S^a, non-microporous surface area, S_n^a, micropore volume, V^a, and the pore width, W^a. The first and the second were calculated from the slopes of the initial and latter linear portions, and V^a from the intercept of the latter linear section with the V_{ads} axis. Pore width of W^a is equal to twice of the value

of α at the breaking point between the linear sections, and denotes primary filling of micropores. The t-method plots the amount of N_2 adsorbed as liquid, V_{ads} , against the corresponding multilayer thickness, t , calculated from the standard isotherm with a non-porous reference solid ^[16]. Similar four α_s parameters were evaluated S^t , Sn^t , V^t , W^t .

FTIR spectra were recorded between 4000 cm^{-1} and 400 cm^{-1} using a Matson 5000 Spectrometer. Discs were prepared by first mixing of 1 mg of dried carbon sample with 500 mg of KBr (Merck, for spectroscopy) in an agate mortar and then pressing the resulting mixture at 5 tonnes cm^{-2} for 5 min, and at 10 tonnes cm^{-2} for 5 min under vacuum. Scanning electron microscopy (JEOL JSM-6400) was used to examine the carbon surface for five samples: the raw cotton-stalks, char C550, P50, K21, and S700 for the sake of comparison. Thermogravimetry was performed using a Perkin-Elmer 7 series thermal analyzer at heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The tracings were recorded (TG and DTA) for two samples: precursor (cotton-stalk straw) and another the precursor treated with H_3PO_4 in 1:1 (w/w) ratio.

3. Results and discussion

3.1 General considerations in porosities of the resulting carbons

Fig 1 shows N_2 adsorption isotherms conducted at $-196\text{ }^\circ\text{C}$. The isotherms change from a type I to probably a mixed of type I and type IV as discussed by Sing ^[7]. The isotherms, for most of the carbons studied, exhibited hysteresis loops of small area at high relative pressure. Various interpretations on hysteresis loops in N_2 adsorption isotherm have been proposed. Among them, appearance of a hysteresis loop due to the presence of ink-bottle type pores is widely accepted, especially for phosphoric acid-activated carbons ^[17]. In the same context, the absence of a plateau and the continuous rise of the α_s plots (Fig. 2) and t-plots (not illustrated) indicates that a considerable fraction of the acid-carbon surface is located in mesopores. For char sample, C550, in particular, both plots exhibit a negative deviation at lower α_s and t values. This might indicate the presence of primary and secondary micropore filling mechanisms ^[18]. The estimated textural parameters evaluated from both Langmuir and BET equations as well as both α_s and t-plots are summarized in Tables 2 and 3. Inspection of these tables reveals that the values of S^a and S^t are comparable in most cases, and appear to measure much higher values than SBET. This finding may be attributed to the narrow range of relative pressure in which the BET equation is applied. Moreover, the BET is applied with great reservation when the majority of adsorbents are located in a microporous area. It is also notable that the BET C values, Table 1, is often quoted as providing a suitable guide to the applicability of the BET method with values greater than 150, as most cases here, implying that the method is not wholly reliable ^[5]. The Langmuir equation is based on the assumption of a homogeneous micropore type, and

that is not the case here. So, probably this method is not also entirely reliable. It seems also that all the values of surface areas calculated by α_s plot, S^a , are intermediate between the values reported by other methods. Consequently, the α_s plot was taken as a high resolution and reliable method, giving more true values for the fitted textural parameters compared with the other results obtained here.

3.2 Porosity development of the chemically activated carbons (H₃PO₄ or KOH)

H₃PO₄, acted as an efficient activating agent for the investigated stalks. Big surface areas products have been obtained of S^a , between 772 and 902 m²/g. Enhanced mesoporosity accompanies raising impregnation ratio from 0.5 to 1.0 as evident from the increase in their contents of V%_{mes} that located between 41.6-48.7 ml/g (Fig. 3). Moreover, the increase in their mean pore radius r^- (nm), non-microporous surface area S_n^a and pore width W^a (Å) offers additional proofs indicating a development in mesoporosity by increasing acid concentration. It appears also that phosphoric acid in a ratio 3:4 is most potentially effective in producing activated carbon than the other two ratios, 1:2 and 1:1. It achieved surface area S^a , of 902 m²/g, and total pore volume VP, of 0.731 ml/g. It is clearly shown from Tables 2 and 3 that the increase in H₃PO₄ concentration much increased the S^a values of the resulting carbon reaching a maximum limit at the ratio 3:4 (sample P34). The increase of the acid concentration above this limit brought about a decrease of about 15% of its S^a , as displayed by P11 carbon. The observed decrease in the S^a of P11 sample due to increasing the H₃PO₄ content could be attribute the possible formation of phosphates via interacting with the inorganics present under pyrolysis action, that may block some pores present ^[9]. This assumption will confirmed latter by FTIR spectra through appearing phosphate band. The action of this acid on the lignocellulosic material can expected as the following mechanism. During impregnation stage the acid attacks the cellular structure of cotton stalks, producing cleavage to the linkages between the lignin and cellulose. This followed by recombination reactions in which larger structural units and strong cross-linked solid are formed ^[9,13,14]. Such effects will naturally be governed and intensified by the acid concentration, as matching with the obtained results here. Accordingly, this acid works, principally, in early stage during impregnation and may be extend to has a slight effect in the carbonization stage.

Unlike the acid-activated carbons, isotherms obtained from the KOH activated carbons show the Langmuir type adsorption, Fig. 1. Based on this observation, the KOH-carbon series are considered as microporous solids having a relatively small external surface areas (S_n^a , 22-27 m²/g) Table 3. This finding is further confirmed by studying the distribution of pore volume within different pore sizes for all obtained carbons, Fig. 3. The figure shows that KOH-carbons were mainly composed of micropores. The data listed in Tables 2 and 3 indicate that KOH series in contrast to the acid series where surface area S^a values are gradually increased from 503 to 1307 m²/g with the KOH/ stalks

ratio. However, the V% mic display an irregular dependence on the KOH/stalk ratios. This may be due to the KOH-carbon washing process. Since in KOH activation, K_2CO_3 and other related compounds are formed after pyrolysis process, these salts will be leached out by 0.1 mol. HCl to form micropores within carbon matrix ^[10, 19]. These findings were confirmed, thereafter, by SEM and IR analyses which evidenced that trace amounts of phosphate and potassium carbonate still contained in the carbon matrix even after intensive and repeated washings. From Table 3 and Fig. 3, among the KOH series and other investigated samples, the higher KOH/stalks ratio via K31 sample, reported much higher surface area amounted to 1307 m²/g and micropore percent reach up to 92.0. This behaviour can be explained as follows: Potassium hydroxide, especially at higher impregnation ratios, work through two competing mechanisms of pore evolution in the carbon structure. The first one is the micropore formation which starts with the addition of KOH to the raw material and the second one is the gasification of the surface carbon atoms through oxidation reaction at higher temperature, 700°C. Both mechanisms leading to creation of abundant of micropores ^[19]. On contrast to KOH, H₃PO₄ in principal plays before carbonization through dehydration and condensation reactions and its response to activation generally decrease with the carbonization of the precursor ^[13]. Thus one can conclude that KOH plays positive effect before and during carbonization while H₃PO₄ plays a positive effect just before carbonization and has, probably, a slight negative effect during carbonization. Therefore, on the basis of this work and our previous works ^[2, 10, 14], among the used of dehydrating agents, KOH, ZnCl₂ or H₃PO₄; activation with KOH is recommended for production of high-porosity carbon from cotton stalks.

3.3 Porosity development of the physically or thermally activated carbons

Pyrolysis of cotton stalks, in presence of a flow of pure steam, enhances carbon porosity within micropores as evident from Fig. 3. With reference to this figure, it can be clearly seen that the micropore fraction represent the major part in both steam samples S600 and S700. Their micropore contents measured 78.6 and 79.7% from their total pore volumes, respectively. It is also very evident that pyrolysis in steam is temperature-dependent, such that reaction at 600°C exerts a very limited effect in developing porosity. Increase the temperature from 600 to 700 °C, led to a tremendous increase in the porous structure. Where the surface area is near to double and the total pore volume indicates about 62% increase. This behaviour can be explained as follows: first assumption, the temperature of 700 °C has the potency to promote steam-internal diffusion and thus enable bulk gasification of the disorganized carbons. Second assumption, superheated steam led to (i) complete removal and cleaning to all volatile products and thus increase both aromaticity and porosity (ii) it initiates and enhances the selective gasification of the active mass (iii) it preserves as well the original botanical morphology as confirmed in the next section by SEM images.

3.4 SEM analysis of Microstructure

SEM images of the microstructures of the raw cotton stalks and their char as well as some selected activated carbon samples, P34, K21 and S700 are shown in Fig. 4. (a to e). For the raw cotton stalks, the surface is relatively organized without any pores except for some occasional cracks. Hydrolysis at 550 °C for 3 h produced a char with undulating surface (Fig. 4 b). There are many rudimentary fine pores within the structure due to the release of volatiles. It is also noticed that there is a clear shrinkage and disintegration of the big grains to small ones after carbonization. The SEM images of the three activated carbons P34, K21 and S700 show that the external surfaces for these carbons are full of cavities and quite irregular as a result of activation. Better information may be obtained from the image of the high magnification of P34 sample, Fig. 4 (c). It appears that there are many macropores of width > 0.2 mm that might be ink-bottle shaped on the surface of this carbon, indicating the aggressive attack of the reagent with the cotton stalks during impregnation. Those pores resulted from the evaporation of the chemical reagent (H_3PO_4) during carbonization, leaving the space previously occupied by the reagents. The external surfaces of the KOH activated carbon, as shown in Fig. 4 (d), is more intact than that of the other two activated carbons. However, there are numerous cracks and small pits distributed over the surface, indicating the severe interaction of the KOH with the stalks during carbonization. The appearance of white spheres in the micrographs of both chemically activated samples, P34 and K21 may be attributed to the presence of phosphate and potassium salt residues in the carbon matrix. These findings were confirmed in their surface chemistry by FTIR as will be discussed below. An interesting observation comes from the image in Fig. 4 (e) for the steamed carbon sample. The effective attack of steam on the raw precursor was clearly observed, yet we noticed that the morphology of the stalks still relatively retain the cellular structure of the parent material even after intense temperatures.

3.5 Pyrolysis behaviour of the cotton stalks and its acid-treated sample

Fig. 5 (a,b) illustrates the changes in weight as function of heat for both cotton stalks precursor and its H_3PO_4 -treated sample, (a) and (b) respectively. Comparison between the two tracks indicates that although both tracks include three stages of the weight loss yet, surprising changes were observed. Impregnation with phosphoric acid brought about significant modifications to the course of pyrolysis and properties as follows: i) increase the thermal stability of carbon matrix where it shifts the main decomposition peak of the raw material indicating delayed pyrolysis from 347°C to 742°C. ii) it promotes the carbon yield at 500 °C indicates that the acid-treated stalks still preserve 74% of the weight as compared to 31.4% without activant. iii) during the early weight loss, up to 200°C, it promotes the dehydration reactions and bond cleavage, leading to increase in releasing the low

molecular weight volatiles and the tar evolution. Thus a weight loss, in acid treated sample attains 18.9% as compared to 11.2 exhibited by the cotton stalks precursor. These observations corroborate to the most recently postulated mechanism ^[12,20] describing the impact of H₃PO₄ on the botanical structure through the penetration and dissolving some components by breaking chemical bonds. This followed by recombination to form a more thermally stable new polymeric and aromatic structures.

3.6 Surface chemistry

Fig. 6 depicts the FT-IR spectra for the raw cotton stalk, RCS, as well as the samples S700, K21 and P34. These spectra are based on the lignocellulosic structure of cotton stalks. The two main components of cotton stalks are cellulose and lignin. Lignin unlike cellulose is aromatic in character and possesses olifinic carbon double bonds. The expected oxygen function groups in cotton stalks are hydroxyl, ether, carbonyl actoxy and etc. The FT-IR spectra of cotton stalks and their char as well as their chemical and thermal activated carbons are shown in Fig. 6. The raw cotton stalks displayed the following bands: the band at 3495 cm⁻¹ is attributed to O-H stretching in hydroxyl functional groups. The band at 2950 and its shoulder at 2880 cm⁻¹ are ascribed to ν C-H and δ C-H (ν =stretching, δ =bending) absorption bands that may present in methyl and methylene groups in the precursor ^[21,22]. The relative intense band at 1745 cm⁻¹ was ascribed to C=O stretching from keones, aldhydes or carboxylic groups. The bands in the region 1640-1430 cm⁻¹ were ascribed to the skeletal C=C stretching vibrations in the aromatic rings bands. The band at 1260 cm⁻¹ attributed to C-O-C stretching in ethers and later band at 817 cm⁻¹ attributed to out-of-plane bending in benzene derivatives.

Significant changes in the spectra of char, C550, and activated products are observed which, in particular, concern the bands located in the two regions between 3500 and 2800 cm⁻¹ and between 1750 and 1000 cm⁻¹. where a sharp decrease in the bands intensities is noticed in these two regions for all the carbon products. These results suggested that under carbonization and activation conditions many weak bonds disappeared. In same time, the C=C bonds, in the new aromatic structures, were involved in the formation of the oxygen functional groups with C-O bonds. This significant decrease occurred in the bands intensities was found to be depending on the activating agent: S700 > K21 > P34. The sequence appears that steam sample has the highest decrease in their bands intensities. This finding may be ascribed to the higher temperature at which S700 was prepared, 700°C. It could break up the bonds thus leading to partially and/or completely destruction to most surface functional groups ^[22]. Whereas, phosphoric-carbon sample has more intense bands than potassium-carbon sample because its high oxygen contents. Two bands appear at ~ 1195 and 995 cm⁻¹ in the spectrum of phosphoric acid-activated carbon are characteristic to P=O groups and to P=O stretching in linear and cyclic polyphosphate and inorganic species. In same trend, a weak bands at 2600 and 1200 cm⁻¹ in

KOH carbon might be ascribed to the traces of potassium carbonates active centres besides metallic potassium which produced at 700°C and they intercalated to carbon matrix ^[21,22]. This indicates that in spite of the extremely prolonged washing period used, a trace amount of phosphate and potassium remained chemically bound inside the pore structure. From weak to medium two bands appeared in the carbon studied in the region 1740 -1539 cm⁻¹ which ascribed to C=O group and C=C skeletal stretch in condensed aromatic system indicating the development of aromatization as a consequence of carbonization and/or activation.

4. Conclusions

The main conclusions derived from the obtained results can be summarized as follows:

- i) Textural characteristics of activated carbons obtained from cotton stalks were found to be strongly dependent on the activating agent, its concentration and mode of activation.
- ii) KOH was found to be the best activating agent producing active carbon measuring the biggest surface area due to production of microporous solids.
- iii) Steam pyrolysis carried out at 700°C much increased (about 2-fold increase) in the specific surface compared to that measured for the solid activated at 600°C.
- iv) The micropores attained a maximum limit (above 90%) in case of KOH activated samples and measured the smallest value for H₃PO₄ treated adsorbents.
- v) H₃PO₄ activation of the raw material shifted its carbonization process to a higher temperature i.e. increases its thermal stability and delayed its main decomposition peak from 347°C to 742°C.
- vi) Both SEM and FT-IR analyses have shown a good agreement with each other and conform to the suggested mechanism. They clearly shown the opening of pores and the functionalities on the surface. Besides, they confirmed the traces of phosphates and potassium carbonates on the surfaces even after intensive and repeated washings. Cotton stalks are well suited for activated carbon manufacture and their porous structure can be tailored to some extent by varying the activation scheme conditions.

Tables and figures

Sample symbol	Activating agent	Impregnation ratio, agent-to-raw (by weight)	Carbonization temperature (°C)	Carbonization time (h)
C550	–	–	550	3
P12	H ₃ PO ₄	1:2	500	2
P34	H ₃ PO ₄	3:4	500	2
P11	H ₃ PO ₄	1:1	500	2
S600	Steam	–	600	1
S700	Steam	–	700	1
K11	KOH	1:1	700	1
K21	KOH	2:1	700	1
K31	KOH	3:1	700	1

Table 1. Some preparation parameters of variously prepared adsorbents.

Sample notation									
	C550	P12	P34	P11	S600	S700	K11	K21	K31
S_L (m ² /g)	128	883	1016	866	453	666	517	812	1311
S_{BET} (m ² /g)	91	660	770	656	303	507	376	613	997
V_P (ml/g)	0.107	0.460	0.731	0.645	0.177	0.285	0.224	0.446	0.480
r^- (nm)	2.36	1.39	1.90	1.96	1.17	1.12	1.19	1.45	0.96
C_{BET}	51	256	753	704	54	97	123	234	391

Table 2. Textural parameters of variously investigated adsorbents.

Sample notation	t -Plot parameters				α_s -Plot parameters			
	S^t (m ² /g)	S_n^t (m ² /g)	V_o^t (ml/g)	Wt (Å)	S^α (m ² /g)	S_n^α (m ² /g)	V^α (ml/g)	W^α (Å)
C550	90	18	0.0374	2.59	85	29	0.024	8.89
P12	784	124	0.252	7.06	793	164	0.236	7.51
P34	906	310	0.201	6.77	902	285	0.195	7.60
P11	770	244	0.180	6.39	772	316	0.169	8.95
S600	388	91	0.140	7.06	371	33	0.138	8.02
S700	727	86	0.192	5.86	722	48	0.216	7.66
K11	511	67	0.150	6.25	503	26	0.170	8.30
K21	805	100	0.237	7.45	808	22	0.227	8.63
K31	1310	62	0.425	6.87	1307	27	0.443	6.94

Table 3. Textural parameters of the resulting carbons evaluated by application of the t - and α_s -methods.

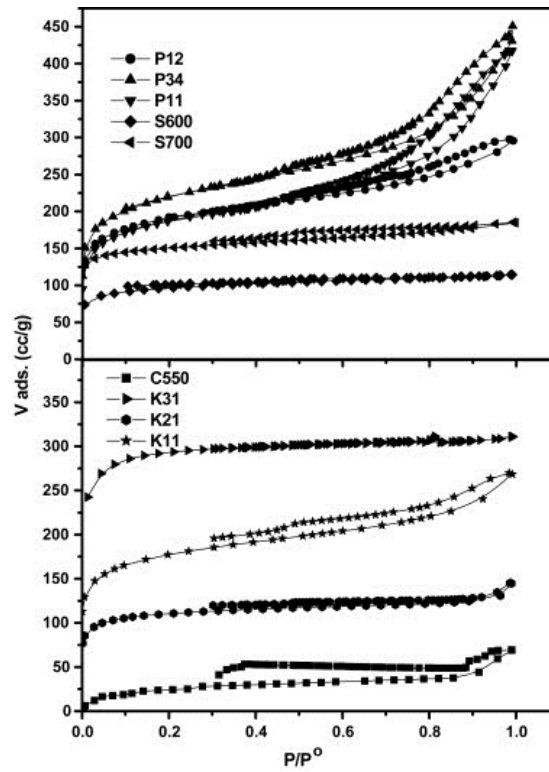


Fig.(1) Adsorption isotherms of N₂/77K by the investigated carbons.

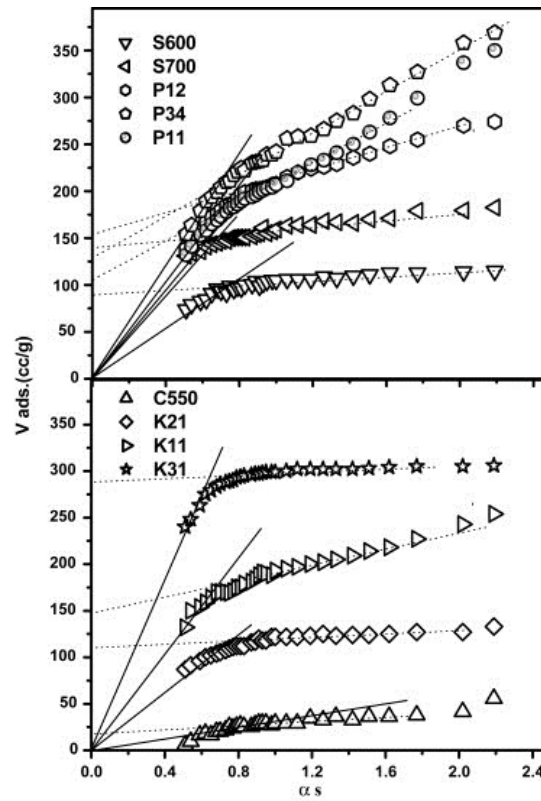


Fig.(2) α_s -plots for N₂/77K-adsorption isotherms of the investigated samples.

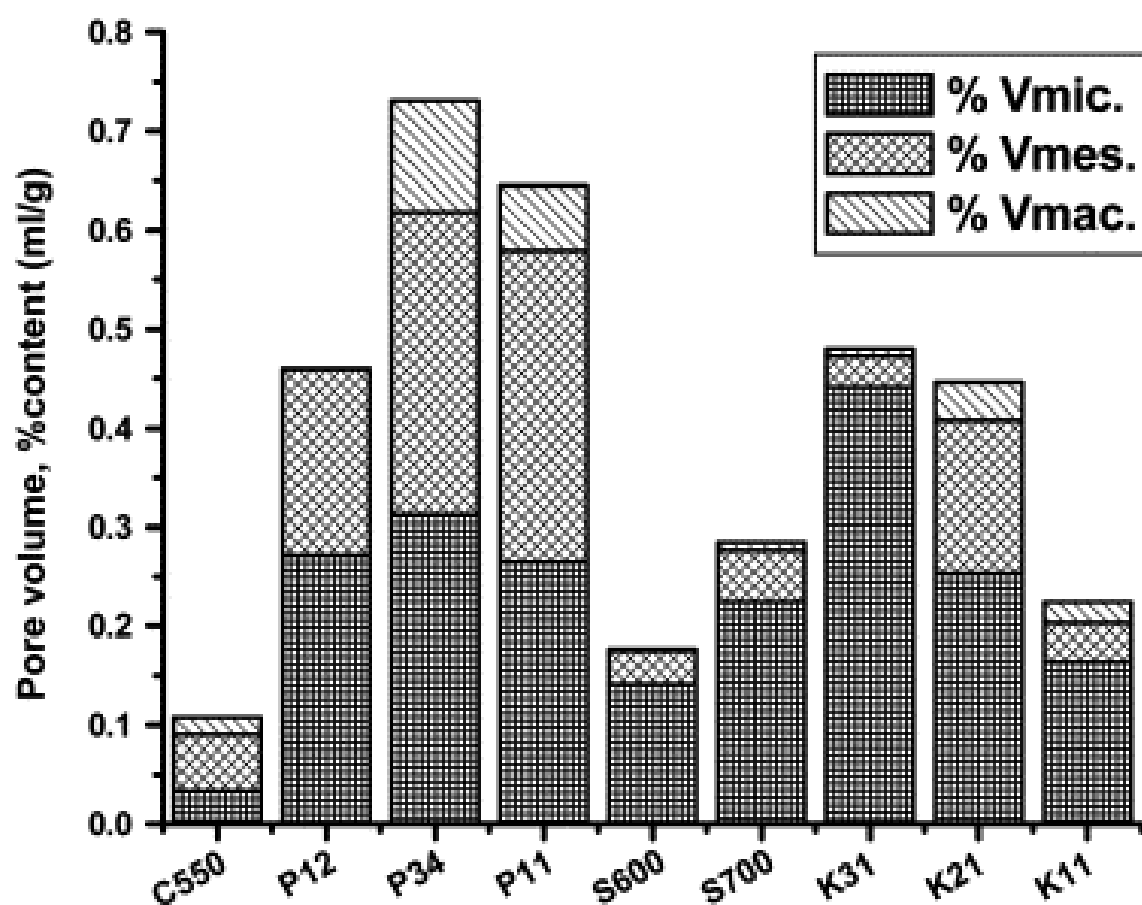


Fig.(3) Distribution of pore volume for the obtained activated carbons within different pore sizes.

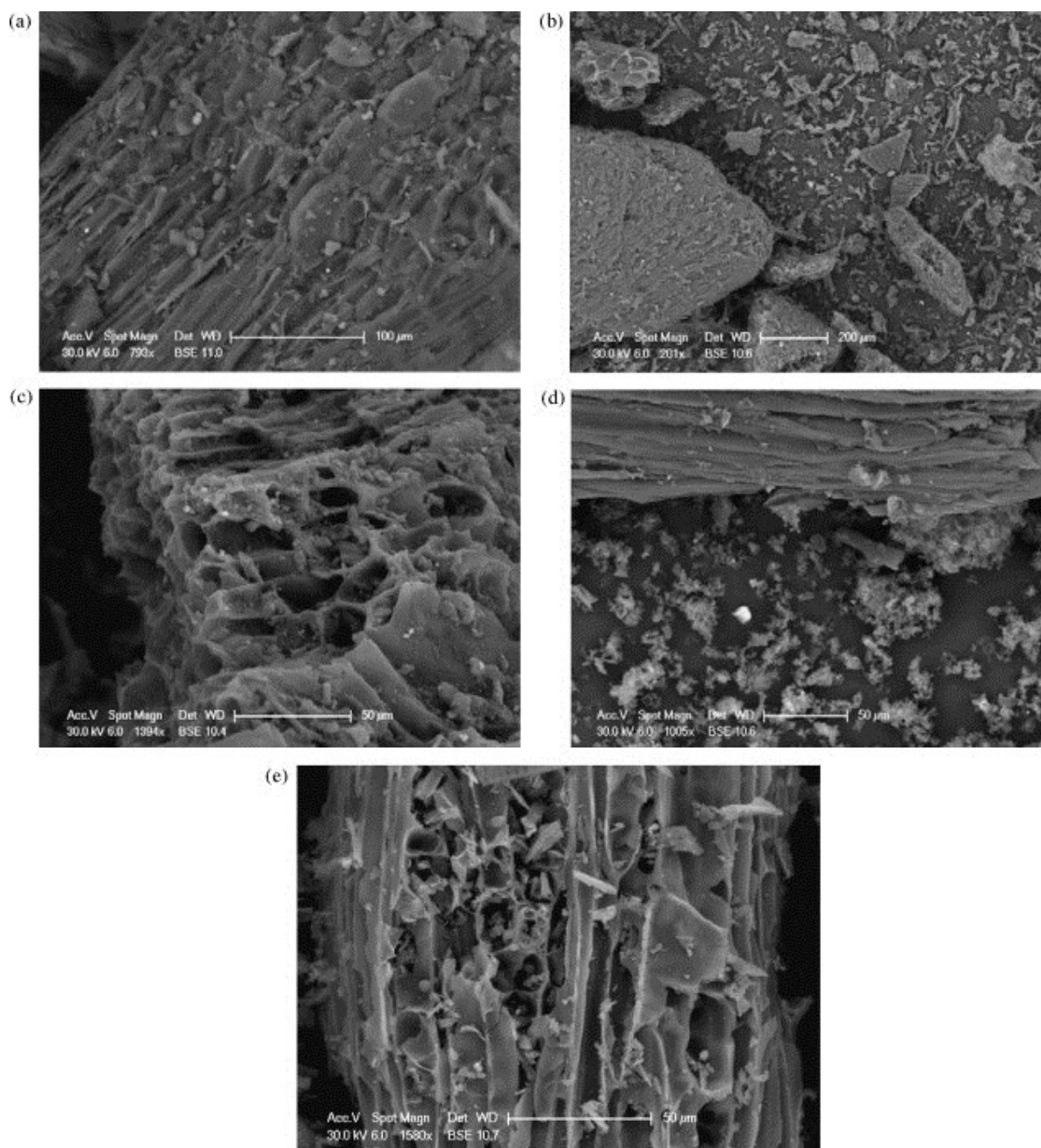


Fig.(4) Scanning electron micrographs of (a) the raw cotton stalks, RCS, and (b) their char, C550 as well as their activated carbons (c) P34, (d) K21 and (e) S700 are shown in a, b, c, d and e, respectively.

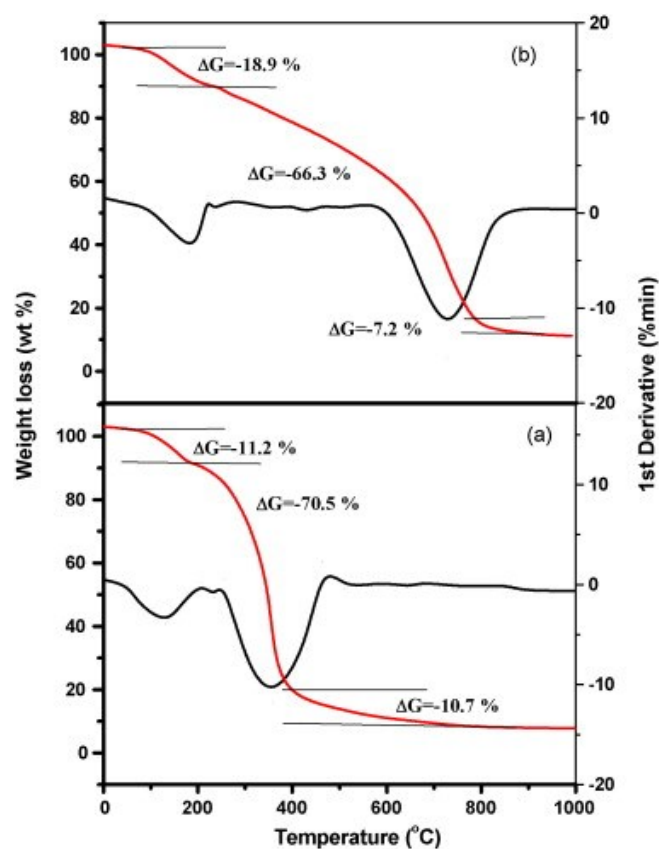


Fig. (5) Thermal behavior (TG and DTG curves) for (a) raw cotton stalks and (b) 1:1 w/w H_3PO_4 -treated ones.

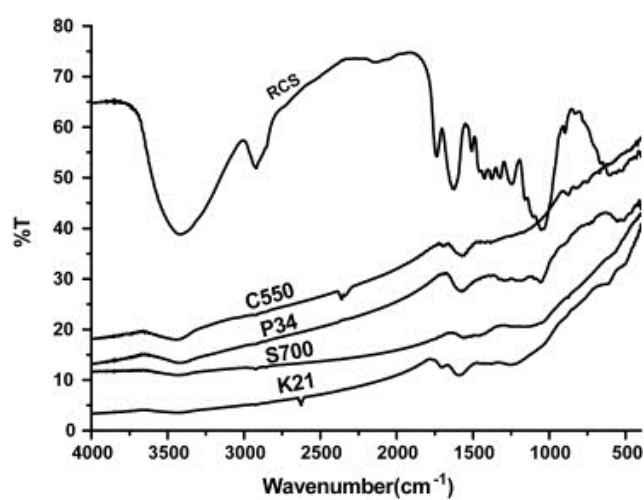


Fig. (6) FTIR spectra for some selected samples.

References

- [1] C.A. Toles, W.E. Marshall, M.M. Johns, *J. Chem. Technol. Biotechnol.* 72 (1998) **255-263**.
- [2] A.A. El-Hendawy, S.E. Samra, B.S. Girgis, *Colloids and Surfaces A* 180 (2001) **209-221**.
- [3] J. Laine, A. Calafat, M. Labady, *Carbon* 27 (1989) **191-195**.
- [4] K. Gerogova, N. Petrov, S. Eser, *Carbon* 34 (1996) **879-888**.
- [5] A. M. Warhurst, G. D. Fowler, G. L. McConnachie, S.J.T. Pollard, *Carbon* 35 (1997) **1039-1045**.
- [6] R.C. Bansal, J.B. Donnet, H.F. Stoeckli, *Active Carbon*, Marcel Dekker, New York, 1988.
- [7] J.W. Patrick, *Porosity in Carbons: Characterization and Applications*, Edward Arnold, London, 1995.
- [8] A. Aygun, S. Yenisoy-Karakas, I. Duman, *Microporous and Mesoporous Mater.* 100 (2003) **189-195**.
- [9] M. Jagtoyen, F. Derbyshire, *Carbon* 36 (1998) **1085-1097**.
- [10] W. Feng-Chin, T. Ru-Ling, H. Chi-Chang, *Microporous and Mesoporous Mater.* 80 (2005) **99-106**.
- [11] A. Attia, A. A. El-Hendawy, S. Khedr, Th. El-Nabarawy, *Adsorpt. Sci. Technol.* 22 (2004) **411-425**.
- [12] G. Yanping, D. A. Rockstraw, *Microporous and Mesoporous Mater.* 100 (2007) **12-19**.
- [13] H. Li-Yeh, Teng. Hsisheng, *Fuel Processing Technol.* 2000; 64: **155-166**.
- [14] A. A El-Hendawy, *Appl. Surf. Sci.* 252 (2005) **287-295**.
- [15] M.J. Selles-Perez, J.M. Martin-Martinez, *J. Chem. Soc. Farad. Trans.* 87 (1991) **1237-1245**.
- [16] B. C. Lippens, J. H. deBoer, *J. Catalysis* 4 (1965) **319-323**.
- [17] W. Feng-Chin, T. Ru-Ling, J. Ruey-Shin, *J. Colloid Interf. Sci.* 283 (2005) **49-56**.
- [18] A. A. El-Hendawy, *Carbon* 41 (2003) **713-722**.
- [19] A. Ahmadpour, D.D. Do, *Carbon* 35 (1997) **1723-1732**.
- [20] A. H. Idriss, D. Jean-Louis, S. Sylvain, L. Marcel, R. Sebastien, *J. Anal. Appl. Pyrolysis* 79 (2007) **101-105**.
- [21] V. Gomez-Serrano, J. Pastor-Viilegas, A. Perez-Florin, C. Duran-Valle, C. Valenzueia-Calahorro, *J. Anal. Appl. Pyrolysis* 36 (1996) **71-80**.
- [22] A. A. El-Hendawy, *J. Anal. Appl. Pyrolysis* 75 (2006) **159-166**.